Supplementary Text S2: Zircon Analytical Methods

U-Pb zircon geochronology: zircon extraction

Twelve samples of intrusive dikes were sent to Overburden Drilling Management (ODM) Laboratories in Ottawa, Canada. Prior to disaggregation, all rock samples are rinsed and scrubbed with a silicone brush to remove any soil or adhering particles.

Samples are ideally disaggregated to 80-90%, -1 mm by electric-pulse disaggregation ("EPD"), however, the amount disaggregated is dependent on: (a) rock type; (b) grain size; (c) and abundance of sulphides, soluble mineral and graphite. The disaggregation chamber is filled with water and a rock sample is placed on a 1 mm sieve. The rock is subjected to pulses of ~200,000 V of electricity.

EPD is much cleaner than mechanical crushing because the disaggregation takes place in water and creates no dust. The disaggregation chamber is lined with a new sample bag for every sample which, along with thorough cleaning procedures, essentially eliminates the possibility of carry-over. A quartz-vein blank is run between every sample. Normally, 1-2 kg of sample is sufficient for most applications. Larger samples may be required if the targeted mineral is not abundant (i.e. in visible concentrations).

The disaggregated samples are pre-concentrated on a shaking table to produce a low-grade table concentrate. Most zircon grains are very small (<50 μm) and are recovered by micropanning the table concentrate. A zircon-rich pan concentrate is produced at this stage.

To concentrate other minerals, the -1 mm table concentrate is sized and further refined by heavy liquid (methylene iodide) separation in to produce a heavy mineral concentrate ("HMC"). The density of the heavy liquid can be lowered to any specific gravity depending on the targeted

mineral. The HMC can be further refined using one or more of the following methods: (a) ferromagnetic separations; (b) electromagnetic separations; (c) sizing (sieving); (d) friction ramp refining; (e) electromagnetic separations; (f) additional heavy liquid separations; and (g) hand-picking of mineral grains.

Seven samples from the twelve sent to ODM labs yielded zircon grain abundances suitable for follow-up U-Pb Geochronology (KZWS-009, KZWS-045, KZWS-010, KZWS-079, KZWS-115, KZWS-130, and KZWS-134).

U-Pb zircon geochronology:

Samples selected for U-Pb zircon geochronology were sent to two labs for different precision analytical techniques in 2017: CA-TIMS (two samples) at Boise State University, Idaho, USA; and LA-ICP-MS (six samples; only five discussed in this paper, as one sample was found to be hydrothermal in origin and yielded insufficient zircons) at the University of Alberta, Canada. Two more samples of intrusive rock were sent to Boise State University for CA-TIMS analysis in 2019 resultant of follow-up sampling in the 2019 field program, guided by better understanding of intrusive phase paragenesis. As a result, the description for CA-TIMS analysis is split into two sections, labeled by year of analysis. Any differences in methodology between 2018 and 2021 CA-TIMS analyses are summarized in the 2021 description.

CA-TIMS 2018 (KZWS-009 and KZWS-045)

Two samples (KZWS-009 and KZWS-045) yielding sufficient zircon grains from extraction at ODM labs were sent to Boise State University, Idaho, USA. The zircons were annealed at 900ºC for 60 hours in a muffle furnace, and mounted in epoxy and polished until their centres were exposed. Cathodoluminescence (CL) images were obtained with a JEOL JSM-

1300 scanning electron microscope and Gatan MiniCL. Zircon was analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) using a ThermoElectron X-Series II quadrupole ICPMS and New Wave Research UP-213 Nd:YAG UV (213 nm) laser ablation system. In-house analytical protocols, standard materials, and data reduction software were used for acquisition and calibration of U-Pb dates and a suite of high field strength elements (HFSE) and rare earth elements (REE). Zircon was ablated with a laser spot of 25 μm wide using fluence and pulse rates of 5 J/cm^2 and 10 Hz, respectively, during a 45 second analysis (15 sec gas blank, 30 sec ablation) that excavated a pit ~25 μm deep. Ablated material was carried by a 1.2 L/min He gas stream to the nebulizer flow of the plasma. Dwell times were 5 ms for Si and Zr, 200 ms for ^{49}Ti and ^{207}Pb, 80 ms for ^{206}Pb, 40 ms for ^{202}Hg, ^{204}Pb, ^{208}Pb, ^{232}Th, and ^{238}U and 10 ms for all other HFSE and REE. Background count rates for each analyte were obtained prior to each spot analysis and subtracted from the raw count rate for each analyte. Ablations pits that appear to have intersected glass or mineral inclusions were identified based on Ti and P. U-Pb dates from these analyses are considered valid if the U-Pb ratios appear to have been unaffected by the inclusions. Analyses that appear contaminated by common Pb were rejected based on mass 204 being above baseline. For concentration calculations, background-subtracted count rates for each analyte were internally normalized to ^{29}Si and calibrated with respect to NIST SRM-610 and -612 glasses as the primary standards. Temperature was calculated from the Ti-in-zircon thermometer (Watson et al., 2006). Because there are no constraints on the activity of TiO_2, an average value in crustal rocks of 0.8 was used.

Data were collected in one experiment in March 2018. For U-Pb and ^{207}Pb/^{206}Pb dates, instrumental fractionation of the background-subtracted ratios was corrected, and dates were calibrated with respect to interspersed measurements of zircon standards and reference materials.

The primary standard Plešovice zircon (Sláma et al., 2008) was used to monitor time-dependent instrumental fractionation based on two analyses for every 10 analyses of unknown zircon.

Radiogenic isotope ratio and age error propagation for all analyses includes uncertainty contributions from counting statistics and background subtraction. For groups of analyses that are collectively interpreted from a weighted mean date (i.e., igneous zircon analyses), a weighted mean date is first calculated using Isoplot 3.0 (Ludwig, 2003) using errors on individual dates that do not include a standard calibration uncertainty, and then a standard calibration uncertainty is propagated into the error on the weighted mean date. This uncertainty is the local standard deviation of the polynomial fit to the interspersed primary standard measurements versus time for the time-dependent, relatively large U/Pb fractionation. This uncertainty is 1.4% (2σ) for $^{206}Pb/^{238}U$. Age interpretations are based on $^{206}Pb/^{238}U$ dates. Errors on the dates are at 2σ.

U-Pb dates were obtained by the chemical abrasion isotope dilution thermal ionization mass spectrometry (CA-TIMS) method from analyses composed of single zircon grains (**Table S2**), modified after Mattinson (2005). Zircon was removed from grain mounts after LA-ICPMS analysis. Grains were selected based on LA-ICPMS dates and CL images.

Zircon was put into 3 ml Teflon PFA beakers and loaded into 300 µl Teflon PFA microcapsules. Fifteen microcapsules were placed in a large-capacity Parr vessel and the zircon partially dissolved in 120 µl of 29 M HF for 12 hours at 190°C. Zircon was returned to 3 ml Teflon PFA beakers, HF was removed, and zircon was immersed in 3.5 M HNO_3, ultrasonically cleaned for an hour, and fluxed on a hotplate at 80°C for an hour. The HNO_3 was removed and zircon was rinsed twice in ultrapure H_2O before being reloaded into the 300 µl Teflon PFA microcapsules (rinsed and fluxed in 6 M HCl during sonication and washing of the zircon) and spiked with the Boise State University mixed ^{233}U-^{235}U-^{205}Pb tracer solution. Zircon was

dissolved in Parr vessels in 120 µl of 29 M HF with a trace of 3.5 M HNO_3 at 220°C for 48 hours, dried to fluorides, and re-dissolved in 6 M HCl at 180°C overnight. U and Pb were separated from the zircon matrix using an HCl-based anion-exchange chromatographic procedure (Krogh, 1973), eluted together and dried with 2 µl of 0.05 N H_3PO_4.

Pb and U were loaded on a single outgassed Re filament in 5 µl of a silica-gel/phosphoric acid mixture (Gerstenberger and Haase, 1997), and U and Pb isotopic measurements made on a GV Isoprobe-T multicollector thermal ionization mass spectrometer equipped with an ion-counting Daly detector. Pb isotopes were measured by peak-jumping all isotopes on the Daly detector for 100 to 160 cycles, and corrected for 0.16 ± 0.03%/a.m.u. (1 sigma error) mass fractionation. Transitory isobaric interferences due to high-molecular weight organics, particularly on ^{204}Pb and ^{207}Pb, disappeared within approximately 60 cycles, while ionization efficiency averaged 10^4 cps/pg of each Pb isotope. Linearity (to ≥1.4 x 10^6 cps) and the associated deadtime correction of the Daly detector were determined by analysis of NBS982. Uranium was analyzed as UO_2^+ ions in static Faraday mode on 10^{12} ohm resistors for 300 cycles, and corrected for isobaric interference of $^{233}U^{18}O^{16}O$ on $^{235}U^{16}O^{16}O$ with an $^{18}O/^{16}O$ of 0.00206. Ionization efficiency averaged 20 mV/ng of each U isotope. U mass fractionation was corrected using the known $^{233}U/^{235}U$ ratio of the Boise State University tracer solution.

U-Pb dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007), $^{235}U/^{205}Pb$ of 77.93 and $^{233}U/^{235}U$ of 1.007066 for the Boise State University tracer solution, U decay constants recommended by Jaffey et al. (1971), and $^{238}U/^{235}U$ of 137.818 from (Hiess et al., 2012). $^{206}Pb/^{238}U$ ratios and dates were corrected for initial ^{230}Th disequilibrium using $D_{Th/U}$ = 0.20 ± 0.05 (1σ) and the algorithms of Crowley et al. (2007), resulting in an increase in the $^{206}Pb/^{238}U$ dates of ~0.09 Ma. All common Pb in analyses was

attributed to laboratory blank and subtracted based on the measured laboratory Pb isotopic composition and associated uncertainty. U blanks are estimated at 0.013 ± 0.009 pg (1σ).

Weighted mean $^{206}Pb/^{238}U$ dates were calculated from equivalent dates (probability of fit (pof) >0.05) using Isoplot 3.0 (Ludwig, 2003). Errors on the weighted mean dates are given as ± x / y / z, where x is the internal error based on analytical uncertainties only, including counting statistics, subtraction of tracer solution, and blank and initial common Pb subtraction, y includes the tracer calibration uncertainty propagated in quadrature, and z includes the ^{238}U decay constant uncertainty propagated in quadrature. Internal errors should be considered when comparing our dates with $^{206}Pb/^{238}U$ dates from other laboratories that used the same Boise State University tracer solution or a tracer solution that was cross-calibrated using EARTHTIME gravimetric standards. Errors including the uncertainty in the tracer calibration should be considered when comparing our dates with those derived from other geochronological methods using the U-Pb decay scheme (e.g., laser ablation ICPMS). Errors including uncertainties in the tracer calibration and ^{238}U decay constant (Jaffey et al., 1971) should be considered when comparing our dates with those derived from other decay schemes (e.g., $^{40}Ar/^{39}Ar$, ^{187}Re-^{187}Os). Errors for weighted mean dates and dates from individual grains are given at 2σ.

U-Pb zircon geochronology: CA-TIMS 2021 (KY19-009 and KY19-017)

The methodology for analysis in 2021 is similar to the process described for 2018 above, with a few differences:

(1) Zircon grains were separated from rocks using standard techniques, instead of through EPD at ODM Labs.

(2) During LA-ICP-MS analysis, zircon was ablated with a laser spot of 25 μm wide using

fluence and pulse rates of 5 J/cm^2 and 5 Hz, respectively, during a 45 second analysis (15 sec gas blank, 30 sec ablation) that excavated a pit ~15 μm deep. This is in contrast to a pulse rate of 10 Hz and ablation pit depth of ~25 μm deep in 2018.

(3) Data were collected in two experiments in January 2021. In addition to the primary standard Plešovice zircon (Sláma et al., 2008), a secondary correction to the $^{206}Pb/^{238}U$ dates was made based on results from the zircon standards Seiland (531 Ma, unpublished data, Boise State University) and Zirconia (327 Ma, unpublished data, Boise State University), which were treated as unknowns and measured once for every 10 analyses of unknown zircon. The secondary correction is thought to mitigate matrix-dependent variations due to contrasting compositions and ablation characteristics between the Plešovice zircon and other standards (and unknowns).

References

Crowley, J.L., Schoene, B., Bowring, S.A., 2007, U-Pb dating of zircon in the Bishop Tuff at the millennial scale: Geology 35: 1123-1126.

Gerstenberger, H., Haase, G., 1997, A highly effective emitter substance for mass spectrometric Pb isotope ratio determinations: Chemical Geology 136: 309-312.

Heiss, J., Condon, D.J., McLean, N., Noble, S. R., 2012, 238U/235U systematics in terrestrial uranium-bearing minerals: Science 335: 1610-1614.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., Essling, A.M., 1971, Precision measurements of half-lives and specific activities of ^{235}U and ^{238}U: Physical Review C, 4: 1889-1906.

Krogh, T.E., 1973, A low contamination method for hydrothermal decomposition of zircon and extraction of U and Pb for isotopic age determination: Geochimica et Cosmochimica Acta 37: 485-494.

Ludwig, K.R., 2003, User's Manual for Isoplot 3.00. Berkeley Geochronology Center: Berkeley, CA, 70 p.

Mattinson, J.M., 2005, Zircon U-Pb chemical abrasion ("CA-TIMS") method: combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages: Chemical Geology 220:47-66.

Schmitz, M.D., Schoene, B., 2007, Derivation of isotope ratios, errors and error correlations for U-Pb geochronology using ^{205}Pb-^{235}U-(^{233}U)-spiked isotope dilution thermal ionization mass spectrometric data: Geochemistry, Geophysics, Geosystems (G^3) 8, Q08006, doi:10.1029/2006GC001492.

Sláma, J., Košler, J, Condon, D.J., Crowley, J.L., Gerdes, A., Hanchar, J.M., Horstwood, M.S.A., Morris, G.A., Nasdala, L., Norberg, N., Schaltegger, U., Schoene, B. Tubrett, M.N, Whitehouse, M.J. 2008. Plešovice zircon — A new natural reference material for U–Pb and Hf isotopic microanalysis. Chemical Geology, 249: 1-35.

Staudacher, T.H., Jessberger, E.K., Dorflinger, D., and Kiko, J., A refined ultrahigh-vacuum furnace for rare gas analysis, *J. Phys. E: Sci. Instrum*., *11*, 781-784, 1978.

Watson, E.B., Wark, D.A., Thomas, J.B. 2006. Crystallization themometers for zircon and rutile. Contributions to Mineralogy and Petrology, 151: 413-433.